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Cobalt(II) complexes of the antibiotic sulfadiazine, the X-ray single crystal structure of $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$

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Abstract

Cobalt(II) complexes of sulfadiazine formulated as $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ and $[Co(C_{10}H_9N_4S)_2(H_2O)_2]$ have been synthesized and characterized by elemental analysis, infrared and UV–Vis spectroscopy and magnetic susceptibility measurements. The crystal structures of the complex $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ and of free sulfadiazine are also reported. The cobalt complex and the sulfadiazine ligand both crystallize in the monoclinic space group, $P21/c$, with sulfadiazine acting as a bidentate ligand. Cobalt is coordinated to two-sulfonamide nitrogen and the pyrimidine nitrogen of the sulfadiazine. Two molecules of methanol complete the octahedral geometry around the cobalt, with interligand hydrogen bonding between methanol and sulfadiazine. Infrared spectroscopy confirmed the presence of water molecule in the coordination sphere of $[Co(C_{10}H_9N_4S)_2(H_2O)_2]$. The electronic spectra and magnetic moments of both complexes were similar, indicating that both complexes have similar structure.

Keywords: Cobalt complexes; Sulfadiazine; Crystal structure; Malaria; Sulfanilamide; Antibiotics

1. Introduction

Sulfonamides are among the most widely used antibacterial agents in the world, chiefly because of their low cost, low toxicity, and excellent activity against bacterial diseases. The clinically useful sulfonamides are derived from sulfanilamide, which is similar to *para*-aminobenzoic acid, a factor required by bacteria for folic acid synthesis [1]. Sulfanilamide was introduced in therapy about half a century ago for prevention and cure of bacterial infections in humans [2]. Its importance was greatly reduced due to the advent of modern antibiotics. Sulfadiazine is a sulfanilamide that is used as an antibacterial as well as an antimalarial drug. Its use as antimalarial depends on its long half-life in the blood of between 60 and 200 h, which obviates the need for frequent administration. However, it is mostly used now in combination therapy with pyrimethamine to treat chloroquine-resistant malaria parasite [3].

Malaria is one of the three major infectious diseases ravaging the world; the others are tuberculosis and AIDS [4]. Despite more than a century of efforts to eradicate or control malaria, the disease remains a major and growing threat to the public health and economic development of countries in the tropical and subtropical regions of the world with 40% of the world at risk of infection [5]. There are an estimated 300–500 million cases, up to 2.7 million deaths and 42 million Disability Adjusted Life Years (Daly's) each year. The mortality levels are greatest in sub-Saharan Africa, where children under 5 years of age account for 90% of all deaths due to malaria [6]. In countries with endemic malaria, the annual economic growth rates over a 25-year period were 1.5% lower than those in other countries. This implies that the cumulative effect of the lower annual economic output in a malaria endemic country was a 50% reduction in per capital GNP compared

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to a non-malarious country [7]. The emergence and spreading of parasites resistant to antimalarial drugs currently in use indicates that novel compounds need development by identification of novel chemotherapeutics targets. The frightening spread of the parasitic resistance has led the World Heath Organization to predict that without new antimalarial drug intervention, the number of cases of malaria will have doubled by the year 2010 [8]. Hence, the search for new antimalarial therapies is a high-priority for the control of the disease.

The use of metal complexes as pharmaceutical has shown promise in recent years particularly as anticancer agents [9]. Research is ongoing in fields such as cancer [10], arthritis [11] and cardiovascular medicine. In the search for novel drugs against chloroquine-resistant malaria parasites, the modification of existing drug by coordination to a metal centre has attracted considerable attention recently [12–14]. Thus, the search for metal-based drug with low level of toxicity and high biological activity against parasites responsible for malaria and chagas disease has gained prominence [15]. Interest in the metal complexes of sulfadiazine is due to its use as pharmaceuticals. Zinc sulfadiazine is used to prevent bacterial infection in burned animals [16] and silvadene (2-sulfanilamidopyrimidine-silver (I)) is used commercially for the treatment of topical burn [17]. The crystal structures of silver sulfadiazine [18], zinc sulfadiazine [19] and cadmium sulfadiazine [20] have been reported. In the silver complex, the active binding sites of sulfadiazine are the pyrimidine N atoms, the sulfonamido N, and one sulfonic O, giving rise to a polymeric arrangement. In zinc(II) compound, one molecule of sulfadiazine coordinates through the sulfonamido N and the other through one N atom of the pyrimidine ring. In the case of the cadmium complex, the cadmium atom lies on the twofold axis and is coordinated to two sulfonamido and amino N atoms from four symmetry-related sulfadiazine anions. The coordination geometry around these metal ions is basically distorted tetrahedral. In our effort to contribute to metal-based drug as alternative therapies in the management of chloroquine-resistant malaria, we present the synthesis and characterization of cobalt(II) complexes of sulfadiazine. We also presented the single-crystal X-ray structures of one of the complexes and sulfadiazine.

2. Experimental

2.1. General procedure

Solvents of analytical grade were used as obtained. Elemental analyses were performed at the micro analytical laboratory, School of Chemistry, the University of Manchester, UK. FT-IR spectra were obtained on a Perkin–Elmer Paragon 1000 FT-IR spectrophotometer in the range 4000–250 cm^{-1}. UV–Vis spectra were obtained on a Perkin–Elmer Lambda 20 spectrophotometer equipped with an integrating sphere for diffuse reflectance spectra. The solution spectra were on DMF solutions. Room temperature magnetic susceptibility measurements were carried out using Sherwood Scientific Magnetic Susceptibility balance using $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were estimated from Pascal's constants [21].

2.2. Synthesis

Sodium salt of sulfadiazine was obtained from Aldrich. The complex was obtained by dissolving (2.723 g, 10 mmol) sodium salt of sulfadiazine in 50 mL of water. This is followed by drop-wise addition of $CoCl_2 \cdot 6H_2O$ (1.186 g, 5 mmol) or $Co(CH_3COO)_2 \cdot 4H_2O$ (1.245 g, 5 mmol) in water with constant stirring at 40 °C for 1 h. A pink precipitate was formed, filtered and washed with water, methanol and diethyl ether successively and dried under a vacuum. Yield: 2.61 g (96%), m.p. 334 °C.

Elemental *Anal.* Calc. for $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$ ($CoC_{20}H_{24}N_8O_6S_2$): C, 40.33; H, 4.06; N, 18.82; S, 10.76; Co, 9.90. Found: C, 40.07; H, 3.92; N, 18.76; S, 10.54; Co, 9.62%. The above procedure was repeated using methanol as the solvent. The product was pale pink in color and

Table 1
Crystal data and structure refinement parameters

	$[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$	Sulfadiazine
Empirical formula	$C_{22}H_{26}CoN_8O_6S_2$	$C_{10}H_{10}N_4O_2S$
Formula weight	621.56	250.28
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	7.1287(9)	13.6830(16)
b (Å)	9.0628(11)	5.8190(7)
c (Å)	20.287(3)	14.7950(17)
α (°)	90	90
β (°)	94.085	115.037(2)
γ (°)	90	90
Volume (Å^3)	1307.3(3)	1067.3(2)
Z	2	4
D_{calc} (Mg/m^3)	1.579	1.558
Absorption coefficient (mm^{-1})	0.871	0.299
$F(000)$	642	520
Crystal size (mm)	$0.35 \times 0.35 \times 0.20$	$0.30 \times 0.20 \times 0.10$
θ Range for data (°)	2.01–26.36	1.64–28.32
Index ranges	$-8 \leqslant h \leqslant 5$, $-11 \leqslant k \leqslant 11$, $-25 \leqslant l \leqslant 25$	$-17 \leqslant h \leqslant 18$, $-7 \leqslant k \leqslant 6$, $-19 \leqslant l \leqslant 16$
Reflection collected	7253	6348
Independent reflections (R_{int})	7256 (0.0000)	2492 (0.0588)
Completeness to $\theta = 26.36$ (%)	99.4	94.0
Data/restraints/parameters	7256/0/192	2492/0/166
Goodness-of-fit on F^2	1.093	0.947
R indices $[I > 2\delta(I)]$	$wR_1 = 0.0433$, $wR_2 = 0.1053$	$R_1 = 0.403$, $wR_2 = 0.0917$
R indices (all data)	$R_1 = 0.0487$, $wR_2 = 0.1081$	$R_1 = 0.0549$, $wR_2 = 0.0966$

is formulated as $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$: $CoC_{22}H_{26}N_8O_8S_2$. Yield: 2.58 g (95%); m.p. = 345 °C. Elemental *Anal*. Calc. for $CoC_{22}H_{26}N_8O_8S_2$.: C, 42.51; H, 4.22; N, 18.02; S, 10.32; Co, 9.48. Found: C, 42.44; H, 4.01; N, 17.92; S, 10.21; Co, 9.35%.

2.3. X-ray crystallography

The crystals for X-ray analyses were obtained by dissolving $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) in 30 mL of methanol and layered with sodium salt (0.545 g, 2 mmol) of sulfadiazine in 50 mL of methanol in a 150 mL conical flask. The mixture was allowed to stand at room temperature for two weeks after which tiny needle-like pink crystals formed. The crystals of sulfadiazine were obtained from a solution of methanol. The data sets for the single-crystal X-ray studies were collected with Mo Kα radiation at 100 K on a Bruker SMART APEX CCD diffractometer equipped with an Oxford Cryosystems low temperature device. For the complex, a semi-empirical absorption correction was applied using SADABS [22] with maximum and minimum transmissions of 0.8450 and 0.7502, respectively; no absorption correction was used for the ligand. The structures were solved by direct methods using SHELXS-97 and completed by iterative cycles ΔF syntheses, using the SHELXTL package [22]. Hydrogen atoms were included in calculated positions and the structures were refined using full-matrix least-squares refinement against F^2 [22]. Crystallographic data are presented in Table 1.

3. Results and discussion

3.1. Synthesis

The sample for the single crystal structure of the ligand was obtained by recrystallization from methanol. Attempts were made to use different metal salts with the intention of establishing the effect of varying the counter-anion on the composition of the complexes, but irrespective of the metal salt used (including halides, acetate, nitrate and sulfate), the product was essentially the same. In each case, two solvent molecules were always accommodated within the coordination sphere of the complex. The formation of the complexes may be represented by the general equation below

$$CoX_2 \cdot nH_2O + 2Na(C_{10}H_9N_4O_2S) \rightarrow [Co(C_{10}H_9N_4O_2S)_2(A)_2] + 2NaX + nH_2O$$

$$(X = Cl^-, NO_3^-, SO_4^-, CH_3COO^- \text{and } A = H_2O, CH_3OH)$$

The complexes were all pink in color and are completely insoluble in water and non-coordinating solvents but are easily soluble in polar solvents such as DMF, with strong donor strength. The complexes were non-electrolytes in DMF with Λ_m values of 2.0 for $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$ and 1.0 Ω^{-1} cm^2 mol^{-1} for $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$, respectively.

3.2. Crystal structures

The molecular structures of sulfadiazine and the complex, $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$, are shown in Figs. 1 and 2 with the atom-numbering scheme used in Table 2, which also contains the most relevant bond distances and angles.

In the centrosymmetric complex, the sulfadiazine behaves as a bidentate anionic ligand. The central ion coordinated via the sulfonamido N and pyrimidine N on each of the sulfadiazine anion, with the fifth and sixth coordination sites occupied by two molecules of methanol. This indicates that in the medium of the reaction, the N(1)–H proton is acidic. The crystal structure of the complex consists of discrete neutral $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ molecules (Fig. 2), which gives rise to network of chains by means of intermolecular hydrogen bonding (Fig. 3). The Co(II) atom has a distorted octahedral coordination in which the sulfadiazine ligands occupy asymmetric positions in the equatorial plane and the methanol molecules, sulfonamide N and the pyrimidine N of each sulfadiazine are *trans* to one another. Selected distances and angles are given in Table 2. The bond lengths between Co(II) and each of the four coordinated N atoms are the same and within experimental error and also the bond lengths of the two coordinated O atoms of the methanol molecules are the same, since they are related by inversion symmetry. The bond distances and angles in this complex are slightly larger, in most cases, than those published for Ag(I) [18],

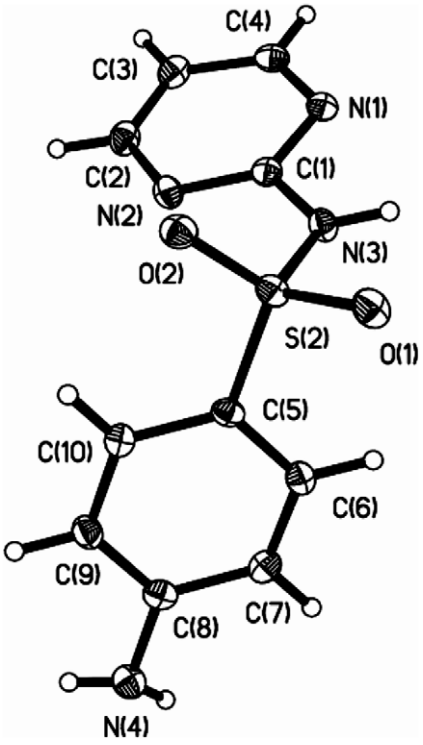

Fig. 1. Molecular structure of sulfadiazine showing the numbering scheme.

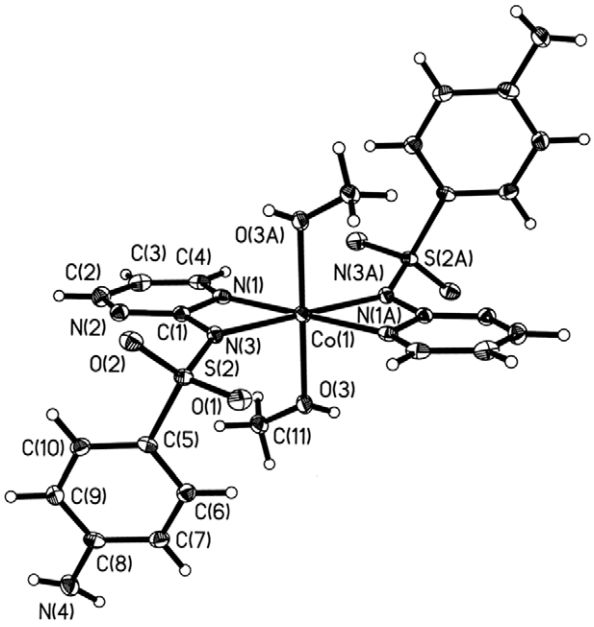

Fig. 2. Molecular structure of $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ with the numbering scheme.

Table 2
Selected bond lengths and angles of $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ and sulfadiazine

Bond lengths (Å)		Bond angles (°)	
Co(1)–N(3)	2.1163(15)	N(3A)–Co(1)–N(3)	180
Co(1)–N(1)	2.1166(15)	N(3A)–Co(1)–N(1A)	62.99(6)
Co(1)–O(3)	2.1377(13)	N(3)–Co(1)–N(1A)	117.01(6)
S(2)–O(2)	1.4411(14)	N(3A)–Co(1)–N(1)	117.02(6)
S(2)–O(1)	1.4420(13)	N(1)–Co(1)–N(1)	180.0
S(2)–N(3)	1.6025(15)	N(3A)–Co(1)–O(3A)	91.16(6)
S(2)–C(5)	1.7593(17)	N(3)–Co(1)–O(3A)	88.84(6)
O(3)–C(11)	1.442(2)	N(1A)–Co(1)–O(3A)	89.26(5)
O(3)–H(5)	0.75(2)	N(1)–Co(1)–O(3A)	90.74(5)
N(1)–C(4)	1.329(2)	N(3A)–Co(1)–O(3)	88.84(6)
N(1)–C(1)	1.364(2)	C(3)–Co(1)–O(3)	91.16(6)
N(3)–C(1)	1.367(2)	N(1A)–Co(1)–O(3)	180
C(11)–H(11A)	0.9800	O(3A)–Co(1)–O(3)	107.12(8)
Sulfadiazine			
C(8)–N(4)	1.383(3)	C(10)–C(5)–C(6)	120.80(17)
C(1)–N(2)	1.345(2)	N(1)–C(1)–N(2)	127.15(17)
C(1)–N(1)	1.381(2)	N(1)–C(1)–N(3)	118.70(17)
N(3)–S(2)	1.6496(16)	N(2)–C(1)–N(3)	114.14(16)
O(1)–S(2)	1.4374(13)	O(1)–S(2)–N(3)	101.73(8)
O(2)–S(2)	1.4282(14)	O(2)–S(2)–C(5)	108.65(9)
C(5)–S(2)	1.7412(19)	O(2)–S(2)–O(1)	119.57(8)

Zn(II) [19] and Cd(II) [20] sulfadiazine complexes, presumably because of the differences in modes of coordination. The packing of the $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ molecules in the crystal structure consists of parallel chains, which are formed by mutual interactions through hydrogen bonding between molecules. Each molecule interacts through 16 hydrogen bonds with five neighbouring molecules (Table 3).

3.3. Infrared spectra

In order to clarify the mode of bonding and the effect of the metal ion on the ligand, the IR spectra of the free ligand and the metal complexes were studied (Table 4) and assigned on the basis of careful comparison of their spectra with that of free ligand. The bands at about 3400 cm^{-1} in the complexes are due to symmetrical and asymmetrical vibrations of the NH_2 group [23,24]. The shift to higher wave numbers in the complexes as compared to the free ligand is probably due to the presence of H-bonding as confirmed by the X-ray crystal structure in one of the complexes. In addition to the three peaks observed in the sulfadiazine, $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$ showed a generally broader band with an additional band at 3558 cm^{-1} attributable to the coordinated water with possible overlaps with

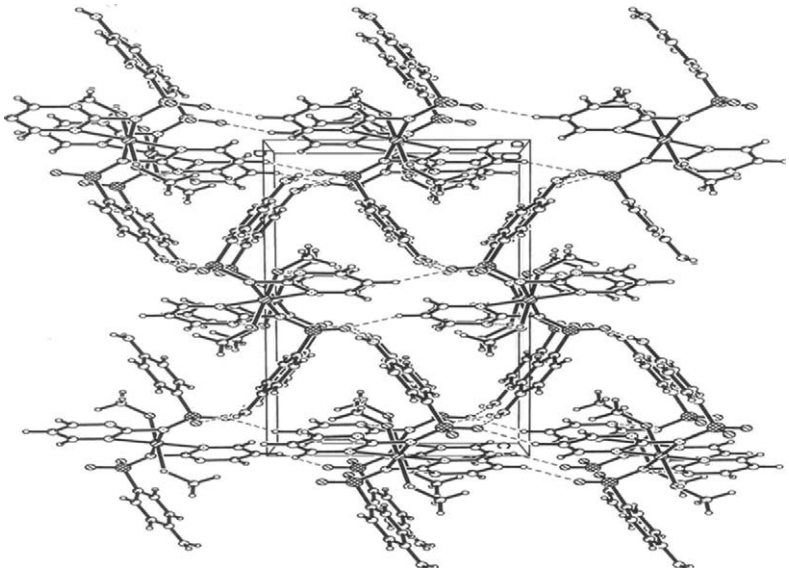

Fig. 3. Packing diagram for $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$.

Table 3
Bond lengths (Å), and angles (°) and position of atoms of hydrogen bonds

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(4)–H(5N)···O(1)#2	0.92(2)	2.08(2)	2.993(2)	172.5(19)
N(4)–H(4N)···O(2)#3	0.85(2)	2.18(2)	3.021(2)	171.5(19)
O(3)–H(5)···O(2)#4	0.75(2)	2.69(2)	3.134(2)	119.6(19)
O(3)–H(5)···N(2)#4	0.75(2)	2.16(2)	2.876(2)	159.0(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+2, -z+1$; #2 $-x, y-1/2, -z+1/2$; #3 $-x+1, y-1/2, -z+1/2$.

Table 4
Selected IR data (cm^{-1}) for sulfadiazine and the complexes

	Sulfadiazine	$[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$	$[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$
$\nu(NH_2)$	3422vs, 3258ms, 3355vs,	3558vs, 3480m, 3378s, 3248m	3431m, 3347s, 3236m
$\nu(C{=}N)$	1652vs, 1580vs	1621s, 1598s	1625w, 1595vs
$\nu(SO_2)_{asym.}$	1325vs	1263vs, 1240vs	1267s, 1251m
$\nu(SO_2)_{sym.}$	1157vs	1124s	1129vs
ν(SN)	942s	1018s, 989vs	987vs
M–N		590vs	588vs
M–O		426s	

Abbreviations: v = very; s = strong; m = medium; w = weak.

the stretching frequencies of the NH_2 group on the pyrimidine ring. The effect of the coordinated metal is also noticeable on the SO_2 symmetrical and asymmetrical stretching modes that are shifted to lower wave numbers (about 33–85 cm^{-1}), while the ν(S–N) shifted by about 47 cm^{-1} to higher wave numbers in both complexes. These observations confirm the coordination of Co(II) through the sulfonamido N atom. The ν(C=N) stretching vibration bands that occur at 1652 and 1580 cm^{-1} in the free ligand shift to 1621–1595 cm^{-1} in the complexes, this supports the coordination of the metal ions through the quinoline N(1) atom. The complexes show medium to weak νCo–N bands between 588 and 500 cm^{-1} and Co–O bands between 450 and 330 cm^{-1}, respectively [23]. $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$ gave an additional intense band at 426 cm^{-1} which is completely absent in $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ probably due to strong coordination of the water molecule as compared to methanol. The bands at 3347–3347 cm^{-1} and those at about 732 cm^{-1} are due to stretching vibration and out of plane bending modes of coordinated water and methanol molecules. The involvement of N and O in coordination is further strengthened by the appearance of bands at 590–297 cm^{-1} assigned to ν(Co–N + Co–O).

3.4. Electronic spectra and magnetic susceptibility measurement

Magnetic susceptibility measurements were carried out on powdered samples at 297 K. The effective magnetic moments, 4.86 B.M. for $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$ and 4.93 B.M. for $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$, are consistent with high-spin octahedral cobalt(II) complexes. The electronic spectra of the complexes in DMF confirmed their octahedral stereochemistry. The electronic spectra of both show two bands of weak to medium intensity at 18,656 cm^{-1} and 22,988 cm^{-1}, respectively, which may tentatively be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_1(P)$ transitions of pseudo-octahedral cobalt(II).

4. Conclusion

The complexes $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ and $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$ have been synthesised and characterised. The structure of $[Co(C_{10}H_9N_4O_2S)_2(CH_3OH)_2]$ was established by single-crystal X-ray, while that of $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$ was inferred from its elemental analysis, conductivity in solution, electronic and IR spectra, and magnetic susceptibility measurements. The IR confirmed the presence of water molecule in the coordination sphere of $[Co(C_{10}H_9N_4O_2S)_2(H_2O)_2]$. The electronic spectra and magnetic moments of both complexes were similar, indicating that both complexes have similar structure.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 271431 for compound $[Co(SD)_2(CH_3OH)_2]$ and CCDC No. 271432 for sulfadiazine (SD). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.).

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